Phase Chemistry of Tank sludge Residual Components

J.L. Krumhansl*, P.V. Brady*, P-C. Zhang*,
H.L. Anderson*, C. Jove-Colon*, M. Nyman*,
J. Liu#, M. Qian#,

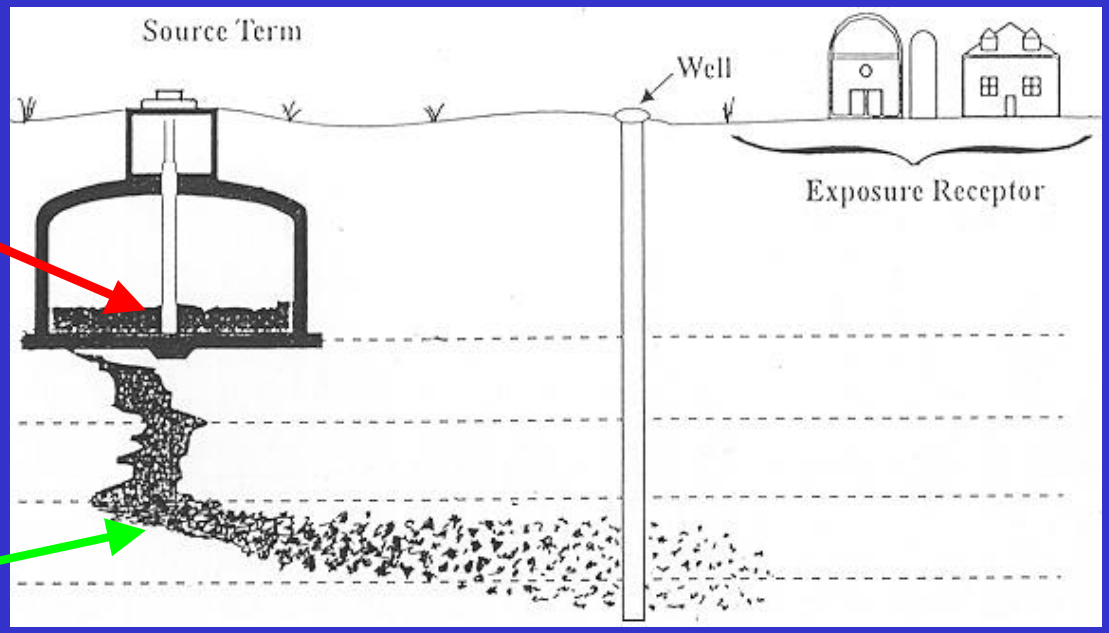
* Sandia National Laboratories, Albuquerque, NM
# Pacific Northwest National Laboratories, Hanford, Wa

QUESTIONS ? PLEASE CONTACT:
JIM KRUMHANSL
(505) 844-9093 (voice) or (505) 844-9093 (fax)
e-mail at JLKRUMH@SANDIA.GOV

This study is directed at developing models describing the retention and release of radionuclides and RCRA metals from the sludges.

Such models are the key to developing cost-effective tank closure strategies

Sludges Left In Tanks Are Sources For Contamination Plumes



A three-step research approach was taken:

1. Process knowledge was used to develop methods for preparing artificial sludges with phases similar to those found in actual tank sludges.

2. Artificial sludges were then doped with non-radioactive radionuclide surrogates.

3. Surrogate release and retention characteristics were then assessed as pore fluid chemistry changed from what is typical of HLW tank fluids to that of more dilute groundwaters.

Hanford wastes came from five major processes

Bismuth Phosphate - Al Clad Fuel
Tributyl Phosphate - Al Clad Fuel
REDOX - Al Clad >> Zr Clad Fuel
PUREX - Al Clad Fuel
PUREX - Zr clad Fuel

Process knowledge indicated that each fuel reprocessing technology partitioned most of the fission products into a single waste stream with a high nitric acid content.

However, studies reported on earlier indicate that several phases dominate sludge phase chemistry:

- Ferrihydrite, and other hydrous mixed oxides
- AlO(OH),
- Apatite,
- Cancrinite Zeolites.

These have been successfully synthesized from the artificial sludge recipes.

TEM/EDS studies indicated that these materials are impure and are likely host phases for sequestering trace elements and radionuclide surrogates.

Simplified Waste Stream Chemistry (molar)

	BiPO4	TBP	REDOX	PUREX	PUREX
	(Al Clad)	(Al Clad)	(Al>Zr)	(Al>Zr)	(Zr Clad)
Al	8E-2	0	1.1	8E-1	0
Fe	3E-2	5E-2	5E-2	1E-1	4E-2
Cr	3E-3	3E-3	7E-2	8E-3	3E-3
Ni	2E-3	2E-3	4E-3	1E-2	1E-3
Zr	3E-4	0	0	0	1E-1
Bi	1E-2	0	0	0	0
Ca	2E-2	2E-2	0	6E-2	2E-2
Si	6E-2	4E-3	4E-2	5E-2	0
F	2E-1	0	0	0	8E-1
P	3E-2	1E-1	0	2E-2	0
Pb	4E-4	1E-4	1E-2	1E-3	0
Mn	7E-3	0	0	3E-2	0
Cd	1E-5	8E-6	0	1E-3	1E-3

TEM/EDS Study of Synthetic $BiPO_4$ Sludge

169 Days at 25°C

Apatite	Ca>Si>P>Al, Fe>Bi
Zeolite	Si>Al>Ca>Na>>Fe>Cd
Fe-Bi oxide	Fe, Ca, Si>Bi>P>Al>>Mn>Cr

169 Days at 90° C

Apatite	Ca>P>>Na>Bi>Pb, Trace Mn, Fe
Bi metal	Bi>>Na, Trace P
Fe-Bi-oxide	Fe, Bi>>Mn, Si, >Al, P, Ca, Na, Trace Pb
$CaSO_4$	Ca, S>>Na
ZrO_2	Zr>>Na
Goethite,	Fe>>Na
Hematite,	Fe>>Na
Zeolite	Al, Si>>Na, Bi, Ca, Fe>Mn, P, > Cr, Ni, Pb

TEM/EDS Study of Synthetic TBP Sludge

(U-Recovery Process)

169 Days at 25° C

Apatite,	Ca,P>>Fe>>Pb, Cr, Na
Ferrihydrite	Fe>>Al, Si, P, Pb, Ca,Cr

169 Days at 90° C

FeOOH(xl?)	Fe>>F>Ca>Si>Ni, Pb
Apatite,	Ca, P > Fe, Na
PbO	Pb>>Fe>Ca

TEM/EDS Study of Synthetic REDOX Sludge

169 Days at 23° C

Boehmite,	Al>Si>Cr, Fe >Ca
Gibbsite,	Al>>Na
Mixed Hydroxide	Al>Fe, Cr>Si>Ca, Trace Pb, Ni
Portlandite	Ca>>Na
Hematite	Fe>>Si, Ca>Pb, Na>Ni

169 Days 90° C

Zeolite	Al>Si>>Ca, Fe, Si>>Cr
Boehmite	Al>>Si, Fe, Cr> Ca>Na>
FeOOH(Xl?)	Al,Fe>Cr>Na, Pb, Si, P>Ni

TEM/EDS Study of Synthetic PUREX Sludge (Al-Clad Fuel)

Later Generic PUREX (NCAW) MIX
266 Days at 90° C

Boehmite	Al>>Fe>>Ni>Cr,Ca,P
Portlandite	Ca only
Hydrotalcite	Al>Ni>Fe>>Cr, Ca

Early PUREX Process
169 Days at 90° C

Boehmite	No EDS taken
Zeolite (good xl)	Al>Si>Na>>Fe, Ca
Apatite,	No EDS taken
FeOOH(xl?)	Fe>>Al>Mn

TEM/EDS Study of Synthetic PUREX Sludge (Zr-Clad Fuel)

169 Days at 25° C

Fluorite	Ca, F>> Na, Zr, Fe >Cr, Si
$NaFeO_2$	Fe, Na>>Zr , Ca, Cr, Ni
Na_2FeF_6	Na, F, Fe>Ca>Cr,,Zr
Na_3ZrF_7	Na, Zr, F >>>Ca, Cr, Fe, Si

169 Days at 90° C

Fluorite	Ca, F, Trace Na, P, Pb
ZrO_2	Zr>>Ca, Fe, Si, Na > Pb
Ferrihydrite	Fe > Ca, F, P , Si, Al, Na> Pb, Ni, Zr,Cs

Tank Closure Operations May Add Other Phases

Likely Filling Materials Include:

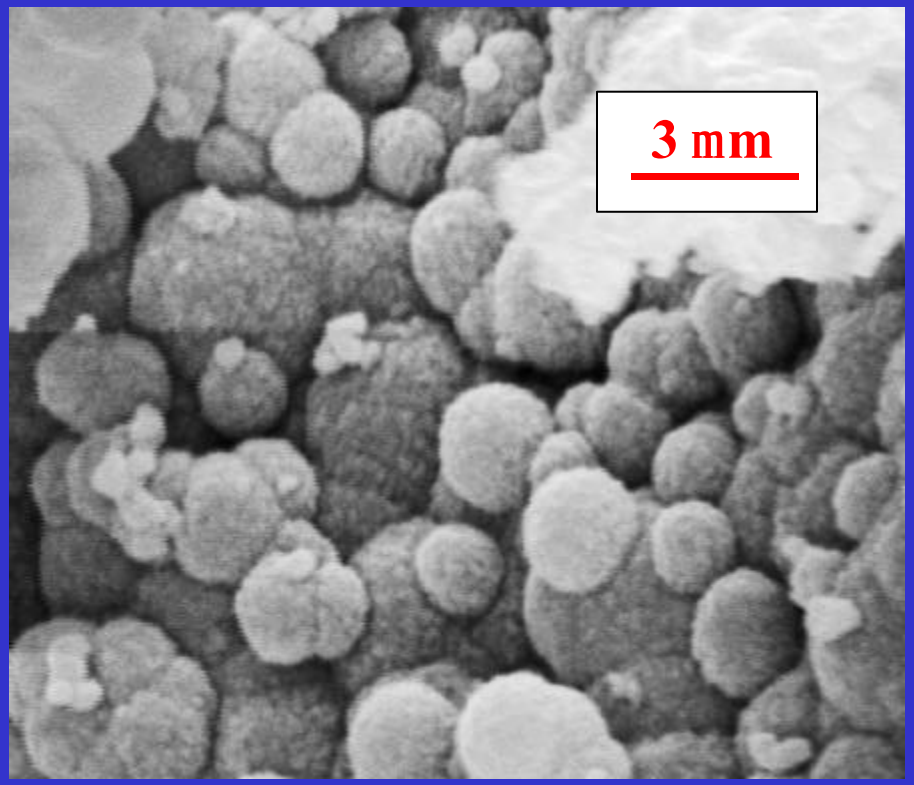
Hanford Soils
Clays- Principally Bentonite

Prolonged exposure to the CO_2 in air may also result.

Accelerated testing assessed what phases may result from interactions between waste fluids these components.

Portland cement will also be added but it is already highly basic and unlikely to react with waste fluids.

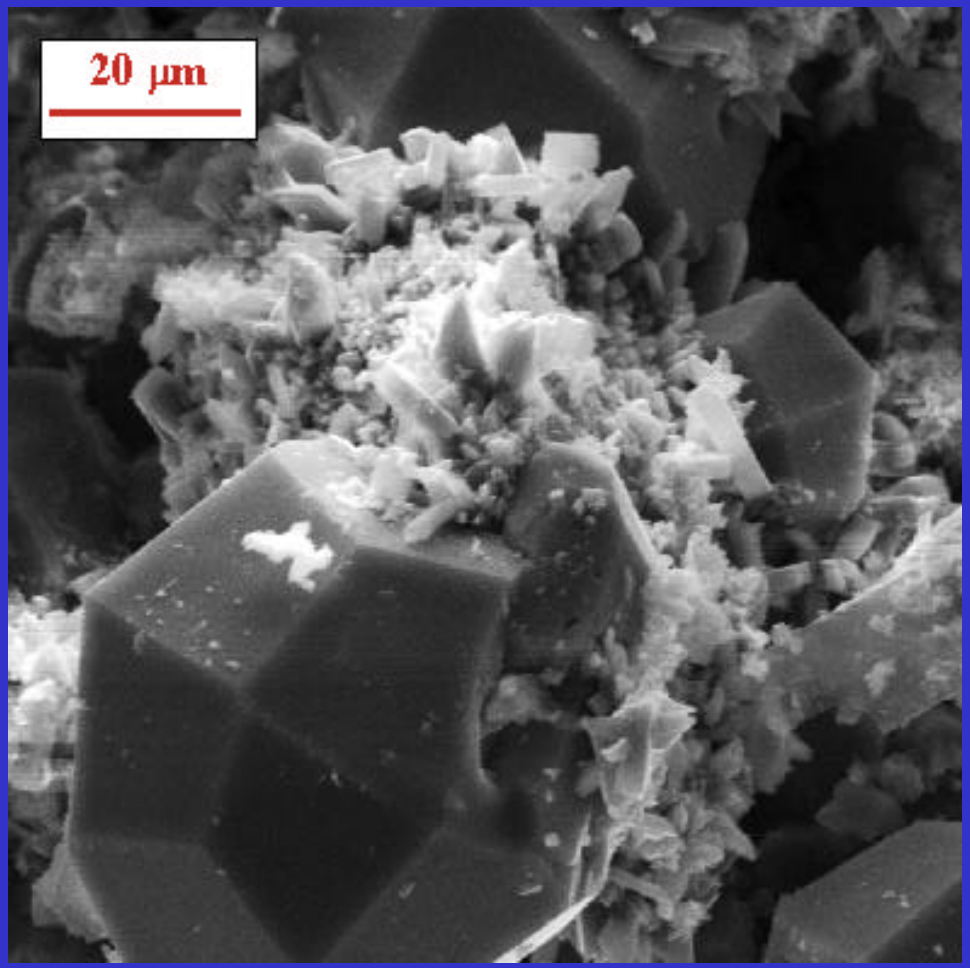
Cancrinite Precipitated on Hanford Soil Grains



Hanford soils reacted with DSSF-7 solution at 90 °C for 82 days

Low temperature soil alteration phases are similar to those observed when tank fluids come in contact with other sources of silica.

At Higher Temperatures Analcime Precipitates



Soil - DSSF-7 Interactions At 200° C

Clay Alteration Products- After Two Weeks In DSSF-7

Mineral	25° C	60° C	90° C
Smectite	All Zeolitized Quartz Gone Clay Gone	Partly Zeolitized Quartz Diminished Clay Gone	All Zeolite Quartz Gone Clay Gone
Illite	No Zeolite Quartz Remains Illite Remains	No Zeolite Quartz Remains Illite Remains	Partly Zeolitized Quartz Remains Illite Remains
Kaolinite	No Zeolite, All Kaolinite	Some Zeolite Some Kaolinite.	All Zeolite No Kaolinite

Relatively inexpensive retention and release testing can be done using non-radioactive surrogates for radionuclides of concern to the public or that performance assessment (PA) has identified as being responsible for most of the far-field dose.

Cs, Sr, Co, and Se have non-radioactive isotopes
ReO_4^- is a good analogue for TcO_4^-
Nd is a good analogue for Am and Cm
Ba is a good analogue for Ra

RCRA metals of concern in the HLW tank waste are Pb and Cr (as $CrO_4^=$)

Radionuclide Analogues In Doped DSSF-7 Solutions After Reactions with Soil and CO_2

Experiment Description	% reduction in supernate concentration		
	Se	Cs	Re
DSSF-7 starting solution 23° C	86 ppm	96 ppm	98 ppm
1) 1:10 soil : solution 90 °C / 2 weeks	12	23	9
2) 0.8:1 soil : solution 90 °C / 2 weeks	16	34	17
3) 1:10 soil : solution 200 °C / 1 week	8	9	10
4) 0.8:1 soil : solution 200 °C / 1 week	17	59	14
5) CO_2 enhanced $Al(OH)_3$ precipitation	21	19	14

Post-Test Solid Radionuclide Surrogate Contents

Experiment Description	ppm radionuclide analogue in experiment solids		
	Se	Cs	Re
1) 1:10 soil : solution 90 °C / 2 weeks	>250	49.4	>5
2) 0.8:1soil : solution 90 °C / 2 weeks	>250	37.5	>5
3) 1:10 soil : solution 200 °C / 1 week	>250	30.3	>5
4) 0.8:1soil : solution 200 °C / 1 week	>250	124	>5
5) CO_2 enhanced Bayerite [$Al(OH)_3$] precipitation at room temperature	8390	9000	8020

Note: before analysis solids were rinsed extensively with dionized water

Mass Balance *

Experiment Description	Se	Cs	Re
1) 1:10 soil : solution 90 °C / 2 weeks	>2.5	0.22	>0.06
2) 0.8:1 soil : solution 90 °C / 2 weeks	>14	0.91	>0.23
3) 1:10 soil : solution 200 °C / 1 week	>3.5	0.42	>0.05
4) 0.8:1 soil : solution 200 °C / 1 week	>14	1.38	>0.28
5) CO_2 enhanced $Al(OH)_3$ precipitation	---	---	---

1. Significant Cs fixation occurred at high solid:liquid ratios.

2. ReO_4^- initially sorbed onto zeolitized sediment was removed by a simple fresh water wash so does not follow other anions (NO_3^-, NO_2^-, $CO_3^=$) into the cancrinite structure.

3. Se behavior is ambiguous.

*** Amount on Solids - AFTER WASHING - /Amount Lost From Solution**

Experimental Studies Directed at Developing Sludge surrogate Release Models:

1. Acid sludge starting solutions were first spiked with about 80 ppm of the surrogates. The pH was then raised to 11-12 to precipitate sludge solids and the sludge was aged for two weeks prior to sampling the fluid.

2. Next, sludge-fluid slurries were dialyzed and titrated with weak acid to lower the pH and ionic strength. At various pH values the fluids were analyzed.

3. At the conclusion of the test the solids were also analyzed

Concentrations (PPM) in Supernate After Two Weeks 25° C Aged Samples

	$BiPO_4$	TBP	REDOX	Al - PUREX - Zr	
Al/Fe#	1.1	0	15.7	12.2	0
Initial	87 ppm	85 ppm	84 ppm	79 ppm	88 ppm
Cr	77	73	108*	9.9	79
Co	<0.40	<0.40	<0.30	<0.30	<0.20
Sr	0.74	1.050	<0.20	<0.20	0.22
Cd	<0.40	<0.40	<0.20	<0.20	<0.20
Ba	7.94	4.67	6.04	4.36	5.69
Nd	<0.40	<0.40	<0.20	<0.20	<0.20
Pb	<0.30	0.57	0.65	<0.20	1.18
Se	73 (-16%)	65 (-15%)	66 (-21%)	53 (-33%)	71 (–19%)
Re	81 (-6.8%)	70 (-16%)	71 (-16%)	67 (-15%)	74 (-16%)
Cs	75 (-14%)	67 (-15%)	97 *	72 (-8.9%)	79 (-10%)

*analytic error, concentration exceeds initial value

based on sludge analysis not initial sludge recipe

Concentrations (PPM) in Supernate After Two Weeks 90° C Aged Samples

	$BiPO_4$	TBP	REDOX	Al - PUREX - Zr	
Al/Fe#	2.0	0	9.1	2.9	0
Initial	87 ppm	85 ppm	84 ppm	79 ppm	88 ppm
Cr	179*	141*	691*	157*	163*
Co	.63	<0.40	<0.40	<0.30	<0.30
Sr	0.88	0.86	<0.40	<0.20	<0.20
Cd	<0.40	<0.40	<0.40	<0.20	<0.20
Ba	8.2	3.2	7.1	5.5	<0.20
Nd	<0.40	<0.40	<0.40	<0.20	<0.20
Pb	<0.30	0.80	1.8	<0.20	<0.20
Se	72 (-17%)	64 (-25%)	65 (-23%)	58 (-27%)	72 (-18%)
Re	83 (-4.6%)	72 (-15%)	77 (-8.4%)	69 (-13%)	80 (-9.1%)
Cs	82 (-5.7%)	77 (-9.4%)	75 (-11%)	72 (-8.9%)	89*

* exceeds initial value, for Cr oxidation to chromate is responsible

based on sludge analysis, not initial sludge recipe

After two weeks at 25° and 90° C.

1. Co,Cd and Nd were quantitatively removed from solution for all five types of sludge.
2. More than 95% of the Pb, Sr and Ba were also removed.
3. Less Ba was removed than Sr.
4. Minor removal of Se, Re (for TcO_4^-) and Cs was noted (Se>Tc>Cs). Neither Se or Re showed any preference for Al-rich sludges.
5. Neither thermal treatment or waste stream chemistry had a large impact on sludge loading.
6. This environment oxidized Cr^{+3} to chromate, which was not effectively scavenged by any of the sludge recipes.

Concentrations (PPB) in fourth dialysis wash
25° C Aged Samples

	$BiPO_4$	**TBP**	**REDOX**	**Al - PUREX - Zr**	
Al/Fe	1.1	0	15.7	12.2	0
Cr	3.2	0.8	46.5	128	2
Co	>0.4	>0.4	>0.4	>0.4	>0.4
Sr	0.8	100	1.3	0.6	208
Cd	>0.4	>0.4	>0.4	>0.4	>0.4
Ba	0.7	34.6	1.3	0.8	18.7
Nd	>0.4	>0.4	>0.4	>0.4	>0.4
Pb	>0.3	>0.3	>0.3	>0.3	>0.3
Se	>4.5	>4.5	8.9	8.0	>4.5
Re	>0.2	>0.2	2.1	0.6	>0.2
Cs	11.6	1.4	132	14.3	0.3
pH	8.9	7.3	10.2	9.8	8.4

Concentrations (PPB) in fourth dialysis wash
90° C Aged Samples

	BiPO4	TBP	REDOX	Al - PUREX - Zr	
Al/Fe	2.0	0	9.1	2.9	0
Cr	7.6	1.8	38.4	75.5	3.9
Co	0.3	1.5	>0.2	0.4	>0.2
Sr	0.8	4.9	36.4	0.5	760
Cd	>0.3	3.1	>0.3	>0.4	>0.3
Ba	0.4	2.1	1.6	0.3	92
Nd	0.4	7.4	>0.2	0.4	<0.2
Pb	0.2	1.7	>0.2	0.4	>0.2
Se	>4.5	>4.5	5.7	39.4	>4.5
Re	2.2	0.2	2.8	12.9	1.0
Cs	13.9	7.5	24.9	26.3	1.9
pH	9.6	8.4	10.0	10.0	7.6

Rradionuclide surrogate releases in low ionic strength mildly basic groundwaters

1. Strongly scavenged surrogates (Co, Pb, Cd, Nd) are only released in very low concentrations (1-10 ppb).

2. Low Al sludges released Sr and Ba in the 30 - 300 ppb range, Sr releases exceeded those of Ba. High Al sludges effectively held Ba and Sr (1-30 ppb releases).

3. Se, Re and Cs releases were higher for the Al-rich sludges. The first rinse (not analyzed) probably scavenged these elements from the Fe rich sludges so only Al-rich sludges retained loadings to be released during later rinses.

4. Treatment temperature did not impact releases.

Concentrations (PPB) in last wash fluids
25° C Aged Samples

	BiPO4	TBP	REDOX	Al - PUREX - Zr	
Final pH	5.9	5.7	5.6	5.6	5.7
Al/Fe	1.1	0	15.7	12.2	0
Cr	3.8	1.6	1030	7.6	>0.3
Co	36.7	567	324	101	256
Sr	1590	2310	2920	2630	704
Cd	65.9	254	488	151	97.7
Ba	767	1080	2250	1560	582
Nd	>0.4	>0.4	42.4	>0.4	>0.4
Pb	<0.3	<0.3	29.8	<0.3	<0.3
Se	>4.5	>4.5	>4.5	>4.5	>4.5
Re	>0.2	>0.2	>0.2	>0.2	>0.2
Cs	204	0.4	137	51.9	0.7

Concentrations (PPB) in last wash fluids
90° C Aged Samples

	BiPO4	TBP	REDOX	Al - PUREX - Zr	
Final pH	6.2	5.1	4.2	4.8	5.5
Al/Fe	2.0	0	9.1	2.9	0
Cr	0.6	0.7	15.6	16.3	>0.3
Co	<0.2	496	195	0.6	76.1
Sr	257	2040	1500	1030	1220
Cd	6.4	908	729	3.1	201
Ba	121	1290	1070	52.8	601
Nd	>0.4	>0.4	1220	>0.4	0.9
Pb	<0.2	0.2	55.6	<0.2	<0.2
Se	>4.5	>4.5	>4.5	6.2	>4.5
Re	0.5	<0.2	<0.2	1.0	<0.2
Cs	83.3	2.7	5.5	40.0	0.3

Last Wash - Neutral to mildly acid pH values

1. TBP and REDOX sludges were least able to retain surrogates

2. 1.0 - 0.1 ppm levels of Sr, Cd and Ba were observed for all sludges while Co, Nd and Pb were significantly less.

3. Cs releases exceeded Se and Re, but all three were probably lost to a significant degree from the sludge before this stage in the washing process.

Post-Leach Sludge Analyses, Depletion and *Enrichment* Relative to Fe - 25° C Aging

	$BiPO_4$	TBP	REDOX	Al PUREX	Zr
pH	5.9	5.7	5.6	5.6	5.7
Al/Fe	1.1	0	15.7	12.2	0
Ba	***1.62***	***3.00***	0.29	0.71	0.67
Sr	0.07	0.71	0.06	0.16	0.07
Pb	0.74	***1.43***	***1.10***	***1.03***	***1.49***
Cd	0.12	***3.31***	0.65	0.90	1.08
Co	0.10	***1.42***	0.96	***1.76***	***1.10***
Cr	0.07	0.89	***1.04***	***1.33***	0.61
Nd	***1.52***	***2.74***	0.99	***2.14***	***1.49***
Re	9E-4	2E-3	3E-3	8E-3	3E-3
Cs	0.01	6E-3	1E-3	4E-3	6E-6

Post-Leach Sludge Analyses, Depletion and *Enrichment* Relative to Fe - 90° C Aging

	$BiPO_4$	TBP	REDOX	Al PUREX	Zr
Final pH	6.2	5.1	4.2	4.8	5.5
Al/Fe	2.0	0	9.1	2.9	0
Ba	***1.37***	0.85	0.49	***1.74***	***1.30***
Sr	0.98	0.13	0.08	1.05	0.20
Pb	0.76	***1.03***	***1.49***	0.88	***1.74***
Cd	0.97	***1.12***	0.61	***1.12***	0.41
Co	0.83	0.84	0.75	0.95	0.88
Cr	0.14	0.28	0.45	0.51	0.37
Nd	***1.01***	***2.39***	0.52	***1.98***	***1.32***
Re	5E-3	4E-3	1E-2	4E-3	7E-3
Cs	0.01	0.02	5E-3	9E-3	4E-3

Solid Sludge Analysis

1. No sludge retained Cs, Re or Se well but Fe-rich sludges did somewhat better than Al-rich sludges for Cs.

2. Heating $BiPO_4$ sludge improved Sr, Cd, and Co retention.

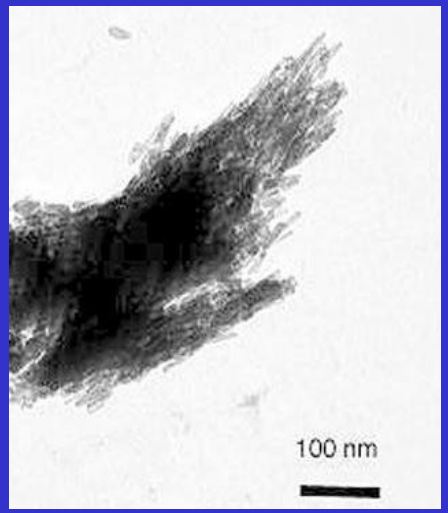
3. TBP and Al-PUREX sludges performed similarly. Most surrogates were well retained but at 25° C Sr was lost.

4. REDOX sludge did not perform as well as TBP sludge. Except for Pb, significant amounts of all surrogates were lost.

5. Zr-Purex sludge was less effective than Al-PUREX.

Apatite "Nuggets" Cause Surrogate Enrichment

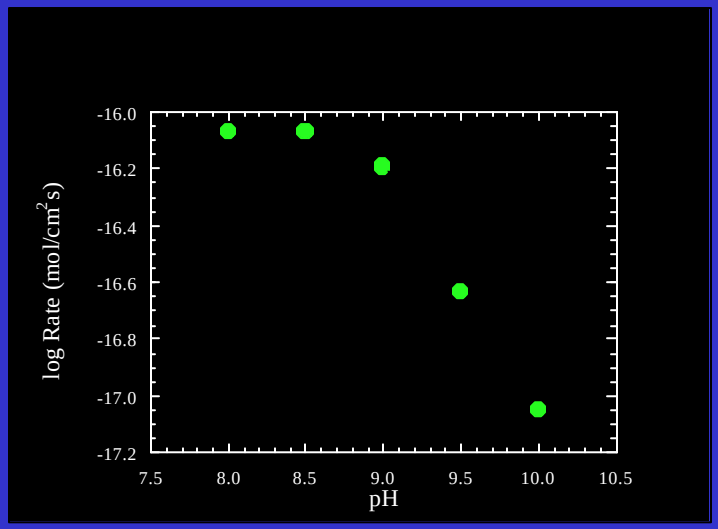
Apatite is a common component in sludges

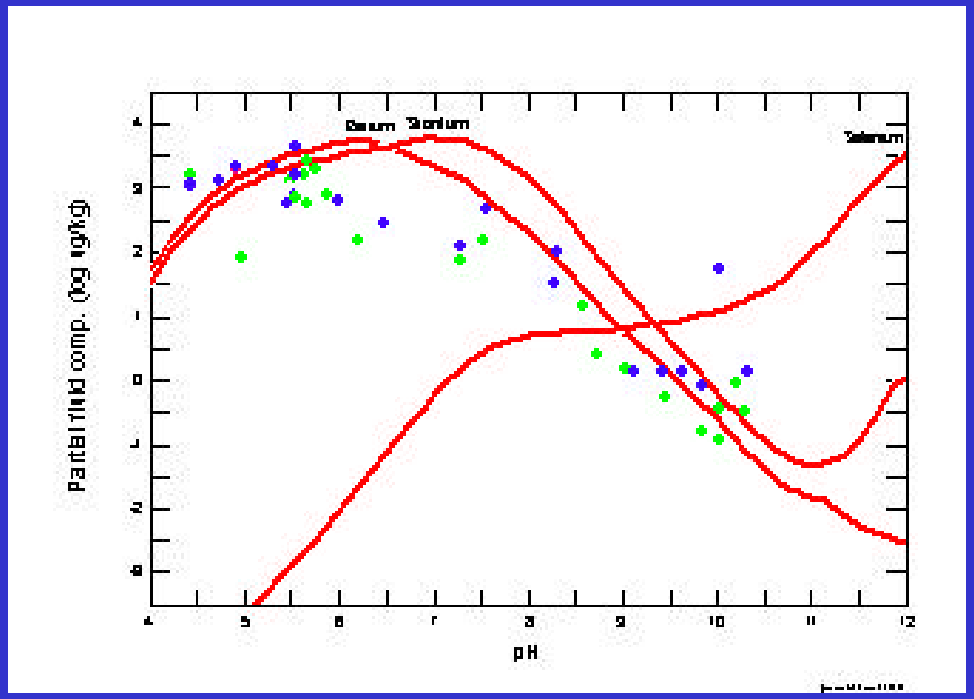


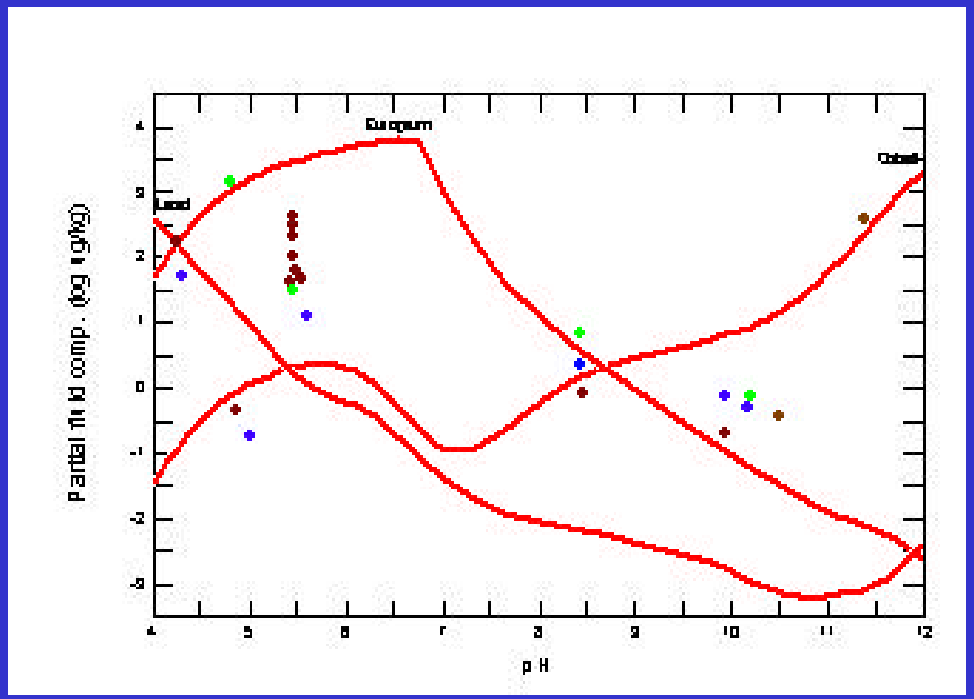
(90°C for 169 Days)

Synthetic (left) and tank sludge (right) apatite crustals

Estimating the release of some radionuclides will depend on quantifying apatite dissolution rates of in various environments. pH is a master variable.







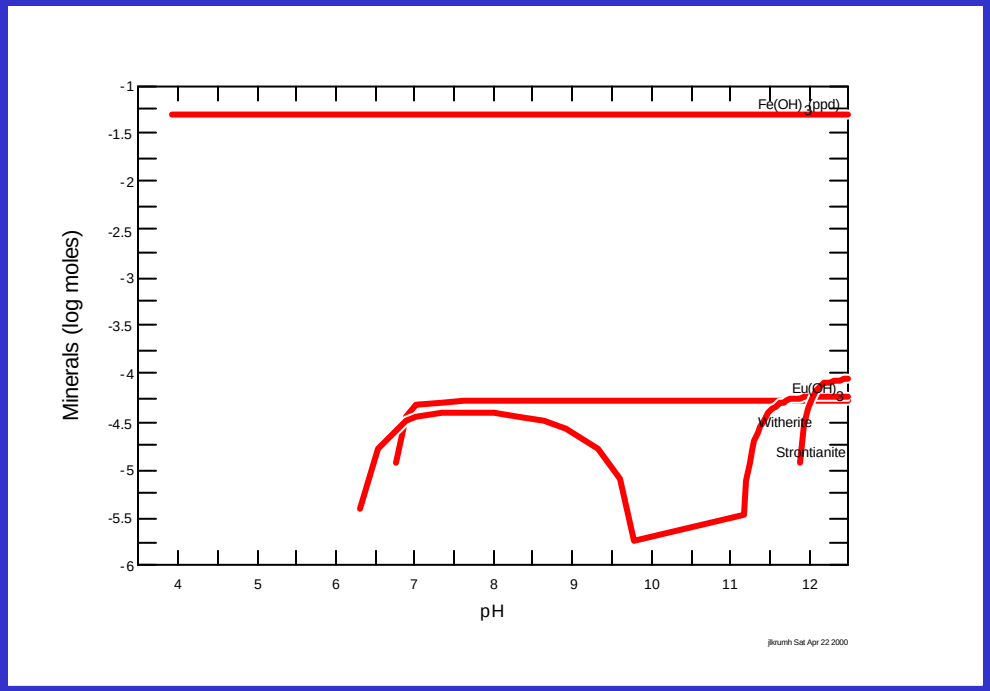
Both desorption and dissolution contribute to solution chemistry

TOP: Aqueous Sr (blue) and Ba (green) are well described.

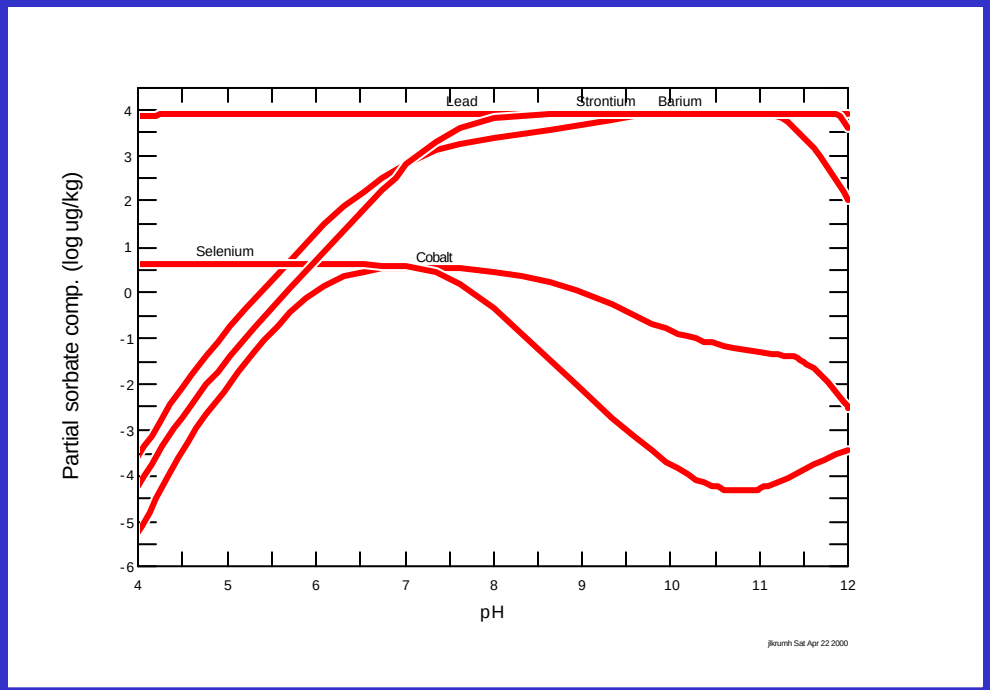
BOTTOM: Co (brown) Eu (green) and Pb (blue) are poorly described.

Processes other than those described by the model operated during the sludge leaching studies.

Geochemical Models Can Differentiate Between Processes:



TOP: Dissolution of minerals as ionic strength and pH decrease.



BOTTOM: Retention and release of sorbed components from hydrous iron oxide as the pH and ionic strength fall.

Future Studies

1. Improve geochemical models:
   Obtain additional parameters for FeO(OH)
   Develop a similar database for AlO(OH)

2. Evaluate higher temperature sludge aging

3. Incorporate organic components in artificial sludge synthesis, aging and release studies

4. Single phase characterization studies concentrating on common sludge phases.

Conclusions

1. The type of sludge in a tank influences radionuclide retention and releases.

2. Likely tank fill materials will not have a large impact on radionuclide releases from sludges.

3. For many radionuclides, much of the inventory will remain in the sludge and not be mobilized into groundwaters.